

PATENT SPECIFICATION

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(54) DETERGENT COMPOSITIONS

(71) We, COLGATE-PALMOLIVE COMPANY, a Corporation organised under the laws of the State of Delaware, United States of America, of 300 Park Avenue, New York, New York 10022, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to detergent compositions, and more particularly to detergent compositions which can be formed into water-soluble (as defined below), spreadable, formstable, solid, optionally transparent, detergent articles such as detergent spotting sticks, to the articles made from such compositions, and to methods for making and using such compositions and articles.

According to one aspect of the present invention a detergent composition capable of being formed into water-soluble (as defined below), spreadable, formstable, solid shaped articles comprises:

- (I) a matrix of (A) a soap component, (B) a synthetic detergent component and (C) a solvent component;

the soap component (A) constituting from 2 to 25% of the matrix and comprising an alkali metal, alkaline earth metal (e.g. magnesium), ammonium or amine salt of a C₈₋₃₀ fatty acid or a mixture of such soaps, the soap component providing in the matrix not more than 20% of salts (other than potassium salts) of fatty acids of 18 or more carbon atoms or not more than 40% of potassium salts of such acids, and wherein the soap has a weighted average carbon content of at least C₁₄, the said carbon content insofar as unsaturated moieties are concerned being calculated on the basis of actual carbon content minus 6;

the synthetic detergent component (B) constitutes from 5 to 88% of the matrix and comprises at least one water-soluble member of the group consisting of anionic organic sulphonates, carboxylates and phosphonates, anionic alcohol sulphates, carboxylates and phosphates, anionic ether sulphates, carboxylates and phosphates, anionic acyl sarcosinates, isethionates and taurides, and nonionic aliphatic detergents, but a maximum of 50% when the synthetic detergent component consists only of anionic organic sulfonates or anionic alcohol sulphates or mixtures thereof;

and the solvent component (C) constitutes from 10 to 70% of the matrix and comprises at least one normally liquid, substantially non-volatile organic solvent having a boiling point of at least about 100°C, at least 10% of component (C) being water-insoluble; and

- (II) a water component (D) constituting from 1 to 35 parts per 100 parts of the matrix.

All percentages and parts throughout this specification are by weight unless otherwise indicated.

Preferably the soap component (A) provides in the matrix not more than 6% of C₂₂ and higher soaps, more preferably not more than 4.5% and most preferably not more than 3%; not more than 8% of C₂₀ and higher soaps more preferably not more than 6% and most preferably not more than 4%; not more than 18% C₁₈ and higher and more preferably not more than 15%.

The composition of the matrix is illustrated graphically by the accompanying drawing which is a ternary diagram wherein the area bounded by the lines connecting the points A, B, C and D represents the limits of the matrix composition and the area bounded by the lines connecting the points E, F, G and H represents preferred matrix compositions.

According to another aspect of the invention a method for preparing the above-defined detergent composition comprises melting the free fatty acids of the soap component (A), mixing the molten fatty acids with the solvent component (C) to produce a homogeneous liquid, and admixing therein, at a temperature above the melting point of the free fatty acids and in the presence of components (B) and (D), sufficient alkali metal-, alkaline earth metal-, ammonium- or amine-salt forming bases to saponify and/or neutralize said fatty acids whereby to form their alkali metal, alkaline earth metal, ammonium or amine salts *in situ*.

The compositions of this invention are preferably shaped, e.g. by pouring the molten composition into a removable mould or the package or container in which it is to be dispensed and/or used and permitting the composition to cool and solidify therein, in the form of a stick of any desired size and cross-sectional configuration, e.g. circular, oval, square, rectangular, triangular or hexagonal. Any other shape may, however, be produced which may be particularly convenient for an intended use. For example, it may be asymmetrical or symmetrical, spherical, cubed, egg-shaped or disc-shaped with a periphery of any desired configuration.

As employed herein, the term "stick" is intended to include the above shaped and indeed any shape of a solid shaped article formed of the detergent composition. The term "spreadable" refers to a firm, solid consistency but readily transferable on to a soiled surface, generally textile, whereon the stick is being rubbed, and excludes articles usually regarded as hard or hard-surfaced. Further, although the compositions and sticks of this invention contain a significant proportion of water-insoluble solvents, the term "water-soluble" applied thereto means that the film or layer of such composition locally applied to the soiled surface is so readily dispersible in the subsequently employed aqueous laundry detergent bath or system as to be effectively water-soluble. By the term "formstable" is meant the physical state of stability of shape under ambient conditions (e.g. 0°C to about 40°C; relative humidity from 0% to 100%) whereby the product does not shrink, expand, deform or flow to any significant degree.

In addition to enabling the attainment of the desirable aesthetic appeal of clear, colourless or coloured transparency, the detergent sticks of this invention have improved properties with respect to water solubility, detergency, solubilization and/or loosening of stains, soils, films and other extraneous undesired material on the surface being treated, and/or stability and resistance to changes in consistency, shape, transparency and surface softness ordinarily caused by environmental conditions of heat and humidity, and loss of volatile components by evaporation. They are exceptionally effective as pre-wash spotters, i.e. for application to local soiled areas of a textile, plastics or other article being cleaned prior to washing the entire article in any desired aqueous hot or cool laundry detergent bath or system. They may be used as pre-dry cleaning spotters, particularly in view of the relatively high content of organic, water-insoluble solvent they may contain.

The compositions of this invention are especially suitable for forming into the desired sticks, since they can be formulated to provide optimum fluidity or viscosity properties when melted prior to the stick-shaping step, and to permit the rapid solidification into stick shape considered necessary to achieve the desired transparency. The method of this invention for making such compositions is relatively simple and expeditious, particularly when employing the more soluble lower molecular weight fatty acids and neutralizing or saponifying them *in situ*.

Subject to the limitations discussed below, the fatty acid employed in making the soaps of component (A) may contain from 6 to 30, preferably from 8 to 22, carbon atoms, may be of animal, vegetable, mineral or synthetic origin, and may be saturated or unsaturated, and straight, mono- or polybranched, chain hydrocarbon carboxylic acids. Illustrative of such acids, there may be mentioned caproic, caprylic, capric, lauric, myristic, stearic, eicosic, oleic, elaidic, isostearic, palmitic, undecylenic, tridecylenic, pentadecylenic, 2-lower alkyl higher alkanoic (such as 2 methyl tridecanoic, 2 methyl pentadecanoic and 2 methyl heptadecanoic) acids. Dicarboxylic acids may also be used, such as dimerized linoleic acid. Other higher molecular weight acids such as rosin or tall oil acid, e.g. abietic acid, may be employed.

For the attainment of optimum solubility, consistency of product, viscosity, melting and solidifying properties, mixtures or blends of the above and other types of fatty acids are preferably employed having an average of at least 12 carbon atoms per molecule and containing no more than 15% of unsaturated fatty acids, no more than 5% of fatty acids containing more than 18 carbon atoms, and preferably at least 5% but no more than 70% or 18 carbon atoms fatty acids, preferably stearic acid. One preferred class of fatty acid blends may, for example, contain 0—5% of C₈, 0—10% of C₁₀, 0—30% of C₁₂, 0—20% of C₁₄, 10—50% of C₁₆ and 5—7% of C₁₈ saturated fatty acids. Readily available commercial blends, and mixtures of such blends for obtaining the most suitable distribution of fatty acids, which may be employed include distilled palm and palm kernel oil fatty acids, distilled coconut oil fatty acids, hydrogenated tallow fatty acids, and commercial stearic acid. The fatty acid contents, in parts by weight, of several such blends, and mixtures thereof, are illustrated in the following Table.

TABLE

	a	b	c	d	e	f	g	h
C ₈	—	4.0	—	2.0	—	2.0	1.3	2.7
C ₁₀	—	3.0	8.6	1.5	—	1.5	1.0	2.0
C ₁₂	—	45.0	66.2	22.5	—	22.5	15.0	30.1
C ₁₄	3.0	19.0	25.0	11.0	—	9.5	8.3	13.7
C ₁₆	30.0	11.0	—	20.5	50+5	30.5	23.7	17.4
C ₁₈	65.0	4.0	—	34.5	43+4	23.5	44.6	24.3
Max. Unsat.	2.0	12.0	—	7.0	4.0	8.0	5.0	8.7

In the above table,

blend a = commercial hydrogenated tallow fatty acids

b = commercial distilled coconut oil fatty acids

c = commercial synthetic fatty acids

d = 1:1 mixture of a and b

e = commercial stearic acid

f = 1:1 mixture of b and e

g = 2:1 mixture of a and b

h = 1:2 mixture of a and b

For the *in situ* saponification of these fatty acids according to the method of this invention there may be employed any alkali metal-, alkaline earth metal-, ammonium- or aminesalt forming base, for example sodium, potassium, magnesium or ammonium hydroxides, mono- di- or triethanol-, or -propanol-, amines, or any other such base yielding a water-soluble salt or soap of the fatty acid being saponified. The base is preferably in the form of a concentrated aqueous solution or dispersion for example of 20 to 49% concentration, and at about the temperature of the molten fatty acid when admixed therewith. An approximately stoichiometric amount of base is preferably employed unless a product is desired containing slight amounts of excess fatty acid or base, e.g. from 0.1 to 5% by weight of free alkali metal hydroxide.

The soap component (A), as well as its known detergent function, contributes body, firmness and non-sticky properties to the detergent sticks of this invention. However, the use of too high a proportion of soap component (A) may unduly raise the melting or fluidizing temperature (to about 110°C or more), the viscosity of the melt and the rate of solidification thereof, thereby preventing proper operation of the stick-making process, and tends to reduce unduly the transparency and rate of dissolution of the resulting stick. The use of too low a proportion of soap component (A), on the other hand, unduly reduces the viscosity of the melt and the rate

of solidification thereof, in addition to yielding sticks which are too soft and sticky at any proportion of components (B) and (C).

The compositions and sticks of this invention contain 2 to 25%, preferably 4 to 15%, and still more preferably 6 to 12%, of soap component (A), of which at least 40% are preferably or equivalent to the alkali metal salts of hydrogenated tallow fatty acids.

As component (B) there may be employed any of the water soluble organic anionic or nonionic aliphatic type referred to above, ample description of which appear in McCutcheon's "Detergents and Emulsifiers", 1969 Annual, and in "Surface Active Agents" by Schwartz, Perry and Berch, Vol. 11, 1958 (Interscience Publishers).

Suitable anionic water-soluble detergents include the alkyl aryl sulphonates, especially the higher (e.g. 10 to 20 or more carbon atom) alkyl benzene sulphonates, preferably those alkyl benzene sulphonates wherein the alkyl group contains 10 to 16 carbon atoms. The alkyl group is preferably linear and especially preferred are those of average alkyl chain lengths of 11 to 14 carbon atoms, such as the linear dodecyl benzene sulphonates.

Preferably also, the alkyl benzene sulphonate has a high content of the 3- alkyl phenyl isomer and a correspondingly low content (well below 50%) of the 2- and 4-alkyl phenyl isomers. One suitable type of such detergent is described in U.S. Patent 3,320,174.

Also, typical of the useful ionic detergents are the olefin sulphonates. Generally they contain long chain alkenyl sulphonates or long chain hydroxy-alkane sulphonates (with the -OH being on a carbon atom which is not directly attached to the carbon atom bearing the $-\text{SO}_3$ group). More usually, the olefin sulphonate detergent comprises a mixture of these two types of compounds in varying amounts, often together with long chain disulphonates or sulphate-sulphonates. Such olefin sulphonates are described in many patents, such as U.S. Patents 2,061,618; 3,409,637; 3,332,880; 3,420,875; 3,428,654; 3,506,580; and British Patent 1,139,158, and in the article by Baumann et al. in *Fette-Seifen-Anstrichmittel*, Vol. 72, No. 4 at pages 247-253 (1970). As indicated in those patents and other published literature, the olefin sulphonates may be made from straight chain alpha-olefins, internal olefins, olefins in which the unsaturation is in a vinylidene side chain (e.g. dimers of alphaolefin), or more usually, mixtures of such compounds, the alphaolefin usually being the major constituent. The sulphonation is usually carried out with sulphur trioxide under low partial pressure, e.g. sulphur trioxide highly diluted with inert gas such as air or nitrogen, or under vacuum. This reaction generally yields an alkenyl sulphonic acid, often together with a sultone. The resulting acidic material is generally then made alkaline and treated to open the sultone ring to form the corresponding hydroxalkane sulphonate and/or alkenyl sulphonate, the number of carbon atoms in the olefin is usually in range from 10 to 25, more commonly 12 to 20, e.g. a mixture of principally C_{12} , C_{14} and C_{16} , having an average of about 14 carbon atoms or a mixture of principally C_{14} , C_{16} and C_{18} , having an average of about 16 carbon atoms.

Another class of useful water-soluble synthetic organic anionic detergents comprises the higher (e.g. 10 to 20 carbon atoms) paraffin sulphonates. These may be the primary paraffin sulphonates made by reacting long chain alpha-olefins with bisulphite, e.g. sodium bisulphite, or paraffin sulphonates having the sulphonate groups distributed along the paraffin chain, such as the products made by reacting a long chain paraffin with sulphur dioxide and oxygen under ultraviolet light, followed by neutralization with sodium hydroxide or other suitable base (as in U.S. Patents 2,503,280; 2,507,088; 3,260,741; 3,372,188 and German Patent 735,096). The hydrocarbon substituent of the paraffin sulphonate preferably contains from 13 to 17 carbon atoms. The paraffin sulphonate will normally be a mono-sulphonate but, if desired, may be a di- tri- or higher sulphonate. Typically, a paraffin disulphonate may be employed in admixture with the corresponding monosulphonate, for example, as a mixture of mono- and di-sulphonates containing up to 30% of the disulphonate.

The hydrocarbon substituent of the paraffin sulphonate will usually be linear but branched chain paraffin sulphonates can be also employed. The paraffin sulphonate used may be terminally sulphonated or the sulphonate substituent may be joined to the 2-carbon or other carbon atom of the chain. Similarly, any di- or higher sulphonate employed may have the sulphonate groups distributed over different carbons of the hydrocarbon chain.

Additional useful water-soluble anionic detergents include higher acyl sarcosinates (e.g. sodium lauroyl sarcosinate), the acyl esters, e.g. oleic acid ester, or isethionates and acyl N-methyl taurides, e.g. potassium Nmethyl lauroyl- or oleyl taurides. Another type of anionic detergent is a higher alkyl phenol sulphonate, for example a higher alkyl phenol disulphonate, such as one having an alkyl group of 12 to 25 carbon atoms, preferably a linear alkyl of 16 to 22 carbon atoms, which may be made by sulphonating the corresponding alkyl phenol to a product containing in excess of 1.6, preferably above 1.8, e.g. 1.8 to 1.9 or 1.95—SO₃H groups per alkyl phenol molecule. The disulphonate may be one whose phenolic hydroxyl group as blocked as by etherification or esterification; thus the H of the phenolic —OH may be replaced by an alkyl e.g. ethyl or hydroxyalkyloxyalkyl, such as a —(CH₂CH₂O)_x H group in which x is 1 or more, such as 3, 6 or 10, and the resulting alcoholic —OH may be esterified to form say a sulphate, e.g. —SO₃Na.

Other suitable anionic detergents are C₈₋₂₀ alkyl sulphates such as lauryl sulphate, tallow alcohol sulphate and alpha or omega-methoxy octadecyl sulphate, and C₈₋₁₈ alkanoyl mono- and diglyceride sulphates and sulphonates.

Still other suitable anionic detergents are the sulphate esters of nonionic detergents, e.g. the reaction products of 1 to 20 moles of a C₂₋₄ alkylene oxide, preferably ethylene oxide, with 1 mole of a C₈₋₂₄ reactive hydrogen-containing compound including aliphatic and alicyclic alcohols such as lauryl, tallow, oxotridecyl, coconut oil and abietyl alcohols, aliphatic dihydric alcohols such as polyoxypropylenated ethylene and propylene glycols, diamines and dithiols, aliphatic and alicyclic carboxylic acids such as stearic acid and abietic acid, aliphatic mercaptans such as dodecyl mercaptan, aliphatic and alicyclic amines such as stearyl amine and rosin amine, aliphatic amides such as stearyl amide, and alkyl phenols such as nonyl and dinonyl phenol.

While the aforementioned types of organic carboxylates, sulphates and sulphonates are generally preferred, the corresponding organic carboxylates, phosphates (see e.g. U.S. Patent 3,595,968) and phosphonates are also useful as anionic detergents.

Generally, the anionic detergents are salts of alkali metals, such as potassium and especially sodium, although salts of alkaline earth metals, ammonium cations and substituted ammonium cations derived from lower (2 to 4 carbon atoms) alkanolamines, e.g. triethanolamine, tripropanolamine and diethanol monopropanolamine, and from lower (1 to 4 carbon atoms) alkylamines, e.g. methylamine, ethylamine, sec-butylamine, dimethylamine, tripropylamine and triisopropylamine, may also be utilized.

Of the anionic detergents the alkali metal salts of sulphated and sulphonated moieties are preferred over the carboxylic, phosphoric and phosphonic compounds.

Aliphatic nonionic detergents operative as or in component (B) include reaction products of from 2 to 50 moles of a C₂₋₄ alkylene oxide, preferably ethylene oxide, with 1 mole of a C₈₋₂₄ reactive hydrogen-containing aliphatic compound, illustrative of which aliphatic compounds are those reactive hydrogen-containing compounds described above as precursors of sulphate esters of nonionic detergents which are aliphatic.

Preferred nonionics surfactants are those represented by the formula:



wherein R represents the residue of a saturated straight or branched chain aliphatic alcohol, preferably a primary alkanol of 8 to 20, more preferably 12 to 18 carbon atoms and n is an integer from 2 to 50, preferably 3 to 20.

Typical commercial nonionic surfactants suitable for use in the invention include an ethoxylation product having an average of 11 ethylene oxide units of a 14 to 15 carbon atom chain fatty alcohol; a 12 to 15 carbon atom chain fatty alcohol ethoxylated with an average of 7 ethylene oxide units; a 16 to 18 carbon alkanol ethoxylated with an average of 10 to 11 ethylene oxide units and such products being variously, or substantially equivalent to the reaction products of 11 moles of ethylene oxide (E.O.) with 1 mole of a C₁₄₋₁₅ primary alkanol or 1 mole of C₁₂₋₁₅ primary alkanol, of 7 moles E.O. with 1 mole of a C₁₂₋₁₅ primary alkanol, and 3:1 to 1:3 blends of the reaction product of 20—50 moles E.O. with 1 mole of a C₁₆₋₁₈ primary alkanol, and of 3—5 moles E.O. with 1 mole of C₈₋₁₀ alkanol.

Other suitable nonionic aliphatic detergents include the liquid and semi-solid

reaction products of 3—20 moles E.O. with 1 mole of C_{11-15} secondary alkanols, the "Pluronics", and the reaction products of 5—7 moles E.O. with 1 mole of C_{16-18} alkane diols (PLURONIC is a trade mark).

Still other suitable aliphatic nonionic detergents are those of the polar type which can also serve to enhance lathering and cleaning properties of other types of detergents, particularly anionic detergents. In a polar type nonionic detergent, the hydrophilic group contains a semi-polar bond directly between two atoms, e.g. $N \rightarrow O$, $P \rightarrow O$, $As \rightarrow O$, and $S \rightarrow O$, the arrow being the conventional representation of a semi-polar bond. There is charge separation between the two directly bonded atoms, but the molecule bears no net charge and does not dissociate into ions. Illustrative types are amine oxides of the formula $R^2R^3N \rightarrow O$ and phosphine oxides of the formula $R^2R^3P \rightarrow O$ wherein R^1 is C_{10-18} alkyl, alkenyl or alkylol and R^2 and R^3 are independently C_{1-3} alkyl or alkylol, for example dodecyltrimethyl amine and phosphine oxides.

As indicated above, mixtures of the above-described detergents may be employed as component (B). It is preferred to use of at least 40% up to 100% of the nonionic reaction product of from 2 to 50, more preferably 5 to 15, moles of ethylene oxide with 1 mole of a saturated aliphatic alcohol, preferably a primary alkanol, of from 8 to 20, more preferably 11 to 16, carbon atoms.

The detergents of component (B) contribute improved hard water solubility and improved detergency to the compositions and sticks of this invention, particularly in hard water and/or with respect to the synthetic fibrous materials such as nylon, polyesters such as "Dacron" and polyacrylonitriles such as "Orlon" and "Acrilan" (DACRON, ORLON and ACRILAN are trade marks). They also increase the water solubility and rates of wetting and dissolution of such compositions and sticks. Component (B) should contain little or no mineral salts, a fairly common ingredient of commercial detergent formulations, to minimize effects on the transparency properties of the products, and may be employed in the compositions and sticks of this invention in amounts ranging from 5 to 88%, preferably 25 to 76% most preferably 35 to 76%.

A major portion ($\geq 50\%$), preferably from 75 to 100%, of the solvent component (C) solvent should be normally liquid, i.e. with a solidification point (S.P.) below 40°C , preferably below room temperature, and a boiling point of at least 100°C , preferably at least 120°C , up to 400°C . It should be substantially non-volatile, with a negligible vapour pressure at room temperature and negligible loss by evaporation on ageing or storage. Thus, particularly good non-volatility is indicated by a loss of weight of 5% or less after 2 hours at 105°C or after 10 hours at 43°C for a 20 grams sample of the solvent in a container with an evaporating surface of about 46.5 sq. cm. (2.3 sq. inches) placed in an oven provided with a flow of air.

Of the non-volatile fraction of the solvent component (C) at least 10% should be water-insoluble (e.g. benzyl alcohol) preferably from 25% to 100%. One or more substantially water-soluble organic solvents, such as propylene glycol, may constitute a part of the non-volatile fraction in an amount not more than 90% preferably not more than 75%, and still more preferably not more than 50% of the fraction. The preferred water-soluble is a dihydric alcohol, such as propylene glycol.

As a suitable substantially water-insoluble organic solvent, benzyl alcohol is preferred, or lauryl alcohol or terpeneol, but as illustrative of other such solvents which may be employed in or as component (C), there may be mentioned, as a rough guide, any such liquid more water-insoluble than benzyl alcohol, including generally any substantially water-insoluble aliphatic, alicyclic or aromatic liquid hydrocarbon, halogenated (iodine, bromine or preferably chlorine) hydrocarbon, hydroxylated hydrocarbon, ether or ester having the abovedescribed properties, for example octane, hexadecane, chlorohexane, chlorobenzene, dichlorobenzene, heptyl, oxotridecyl and hexadecyl alcohols, abietyl alcohol, octanediol, phenethyl alcohol, mono- and di- C_{1-14} alkyl phenols, phenyl ether, benzyl ether, 1,2-dibutoxy benzene, 2-benzyloxyethanol, butyl ether, diethyl- and dibutyl-phthalates, benzyl propionate, and isopropyl myristate, palmitate and stearate. Benzyl alcohol is preferred for providing body and form-stability to the compositions.

Similarly, as a general guide, the substantially water-soluble solvent in or as component (C) may be any such solvent which is more water-soluble than benzyl alcohol. It may be of any type chemically, but is generally a monohydric or polyhydric alcohol, ether alcohol, or amine such as 1,7-heptanediol, the mono- and polyethylene and -propylene glycols which are liquids and are of up to 4000 mole-

cular weight, and the mono-C₁₋₁₄ alkyl ethers thereof, glycerol, diglycerol, 2-pentanol, 1-butanol, mono-, di- and triethanolamine, and 2-amino-1-butanol, especially the polyhydric alcohols and alkanolamines.

As already pointed out the solubility of benzyl alcohol (reported 4g per 100 ml of water at 170°C) is taken as a general guide for distinguishing water-soluble and water-insoluble solvents. As a further guide, a solvent may be considered water-insoluble if its solubility in water at 20°C is less than 10% by weight, preferably less than 5% by weight.

Suitable ratios of water-insoluble to water-soluble solvents fall within the range from 10:1 to 1:10 preferably 10:1 to 1:5 and more preferably 8:1 to 1:3. Other preferred ratio ranges are 5:1 to 1:3 and 4:1 to 1:2.

The solvent component (C) is essential for the production of sticks which are transparent and further functions as a coupling or mutual solvent for the soap component (A) soap and its fatty acid precursor, and the detergent component (B). It also fluidizes the melt and facilitates the shaping thereof into sticks which solidify rapidly on cooling. It improves the surface softness and solubility of the sticks. The use of substantially all water soluble solvent in component (C), while affording good mutual or coupling solvency for components (A) and (B), and good water-solubilizing of the stick products, tends to increase unduly the softness tackiness and hygroscopicity thereof in storage and use, particularly in the case of polyhydric alcohols. Such tendencies can be controlled by limiting the proportion of water-soluble solvents and employing water-insoluble solvents in component (C) as described above, in addition to the other functions performed by such water-insoluble solvents. A controlled degree of hygroscopicity in the products may be beneficial in preventing them from drying out, shrinking and cracking in storage and use. Component (C), like component (B), should of course also be stable and resistant to the action of the base or alkaline material used in making the component (A) soap *in situ* according to the method aspect of the invention.

Component (C) should generally constitute no more than 70%, preferably no more than 60%, still more preferably less than 50%, of the composition and sticks of this invention, to avoid unduly reducing the detergency properties thereof because of the resulting lower proportions of components (A) and (B), and to avoid unduly increasing the sweating (liquid leakage), hygroscopicity, softness and tackiness of the sticks. In general, the compositions and sticks of this invention may contain approximately 10 to 70%, preferably 20 to 60%, and more preferably 20 to less than 50%, of component (C).

Preferably the matrix contains from 0.8 to 5.7 parts of component (B) per part of component (A), from 1 to 8.6 parts of component (C) per part of component (A) and from 0.53 to 6.8 parts of component (C) per part of component (B).

The water component (D) contributes to a lowering of the viscosity of the compositions in the fluid or molten state, and facilitates neutralization of the fatty acid precursors of the soap component (A) *in situ*, in addition to assisting in solubilizing components (A) and (B). Further, some if not all the water is conveniently introduced in the form of an aqueous solution of the base or alkaline material employed in the *in situ* neutralization or saponification of the fatty acid precursors of the soap component (A). Water also increases the water-solubility and transparency of the sticks, and its partial loss from the sticks by evaporation during ageing and storage, particularly from the outer layers of the sticks, is balanced by the hygroscopic tendencies of other components, especially polyhydric alcohols in component (C). Too low a proportion of water detrimentally affects the workability of the compositions and the transparency of the resulting sticks. Too high a proportion of water unduly reduces the rate of solidification of these compositions into sticks, and unduly increases the stickiness and softness thereof. Preferably the amount of water present is from 1% to 15% by weight of the composition.

In general, the compositions and sticks of this invention should contain, per 100 parts of the matrix, 1 to 35 parts, preferably 5 to 15 parts, more preferably 5 to 10 parts, of the water component (D), and may further contain minor proportions, for example a total of up to about 10%, of common additives including colouring materials such as dyes, brighteners or optical dyes, preservatives, u-v (ultra violet) absorbers, stabilizers, perfumes, disinfectants, foaming and lathering agents, enzymes, fillers, sequestrants, soil suspending agents and anti-redeposition agents. Fillers and builders can also be added in any convenient amounts (e.g. 1-85%). Sodium sulphate is a usual filler, phosphates, carbonates, borates and silicates being illustrative of inorganic builders. Among the builders, sodium tripolyphosphate is the usual choice. Organic builders such as trisodium nitrilotriacetate,

hydroxyethyliminodiacetic acid (sodium salt), citrates and gluconates are useful. Polyelectrolytes and sequestration agents can also be used in any desired amounts.

For preparing the compositions of this invention, it is preferred to melt the free fatty acids corresponding to the soaps of the soap component (A) in a heated vessel, mixing in components (B) and (C), and gently stirring the mixture at a temperature above, but preferably no more than 30°C above, more preferably 2 to 15°C above, the melting point of the fatty acids (usually about 70 to 80°C) until a homogeneous liquid is obtained. A solution of the selected salt-forming base in water component (D), preferably at the temperature of the homogeneous liquid, is then mixed therein, preferably gradually and/or in small increments to avoid lumps and overheating, until the *in situ* neutralization and/or saponification of the fatty acids in the liquid is complete. Desirably, an approximately stoichiometric amount of the base is employed to avoid excess base or fatty acids in the product. Neutralization of the product can be ascertained, for example, by periodic testing with phenolphthalein indicator. If desired the detergent component (B) may be first dissolved in the heated solvent component (C) and the resulting solution filtered to remove mineral salts and any other undissolved material prior to mixing the (B) and (C) components, in the form of the resulting hot clear solution, into the molten fatty acids.

After all the base has been added and the resulting hot liquid product mixed sufficiently until it is determined that the acids are neutralized, any desired minor amounts of the above described additives may be mixed in together, if desired with any desired additional amounts of water component (D). Alternatively, some of the water component (D) may be added together with the detergent component (B) and/or the solvent component (C).

In some instances it may be desirable to replace up to 75% or even more of the initially melted free fatty acids by their corresponding soaps or salts, e.g. neat or kettle soap, with of course a corresponding reduction in the proportion of salt-forming base subsequently mixed with the hot melt to neutralize or saponify the free fatty acids therein.

The method according to the invention may be modified when a product is being prepared containing a heat-sensitive anionic organic sulphonate or alcohol sulphate detergent as or in component (B). In this modification the heat-sensitive detergent is not mixed with the molten fatty acids prior to the exothermic neutralization reaction thereof with the base, but is instead subsequently mixed into or with the previously neutralized and cooled liquid (to just above the solidification point of the liquid) containing the soap or fatty acid salt component (A), the solvent component (C) and any remaining detergent portion of the component (B).

The hot melt liquid composition of the invention produced as described above may if desired be cooled and solidified in bulk or any other desired form. For instance, such cooled and solidified composition may be remelted, but preferably the hot liquid composition is employed without such intermediate cooling, solidification and remelting steps, thereby avoiding attendant possible loss of components by decomposition and/or evaporation, but is instead directly poured into moulds, packages or containers of the desired shape and size, e.g. sticks, and cooled to below the solidification point. The improved water-soluble, spreadable, solid, optionally transparent, detergent sticks of this invention are thereby produced and may if desired be aged a short time to permit equilibrium with the environment.

The products of this invention are generally transparent, stable, spreadable, solid, form-stable materials which exhibit excellent detergency in a clothes laundering process and have excellent solubility characteristics particularly in washing machines.

The products of this invention generally have a soil removal ability comparable with, if not superior to presently used clothes laundering detergents. The detergency is conveniently measured by both the standard Tergotometer (U.S. Testing Company, Hoboken, New Jersey, U.S.A.) test and with practical machine washes. In the Tergotometer test an aqueous solution of detergent (0.1—0.5% concentration) is stirred with soiled swatches (and usually with clean swatches as well as for redeposition effectiveness) and the detergency is then conveniently determined by "before" and "after" readings on a colour difference meter (e.g. Gardner Color Difference Meter). The test may be run at any temperature (generally from room temperature to the boil) with stirring at up to 250 rpm, for 5 to 20 minutes (conveniently 10 minutes) at water hardnesses from 0 to 300 or more ppm (as CaCO₃). Prior to the "after" readings, the cleansed swatches are rinsed for

a few minutes in the same hardness water as used in the detergency step, dried and then evaluated.

The products of this invention are outstanding for use on various stains, e.g. grease, oily soil, lipstick and ball point ink. The dissolution speeds of the products of this invention are measured in water at the room temperature to the boil (generally and conveniently at 40°C). The method is generally to add 2 grams of products to 500 ml of water at a selected temperature and stir at selected standardized conditions until all the products is dissolved. The procedure, specifically, is to use a 600 ml beaker of 12 cm height and 8.5 cm in diameter (very flat bottom) graduated every 50 ml. The 500 ml of water is placed in the beaker, the temperature is set, the 2 grams of product is added and stirring is effected by means of a magnetic stirrer which is a cylindrical bar having a 1 mm thick plastics coating. The overall dimensions of the bar are 12 mm diameter and 6.2 mm in length. The speed of rotation is adjusted to give a vortex with its apex at the 300 ml graduation of the beaker.

The products of this invention have dissolution speeds, when measured as described, of from $\frac{1}{4}$ to 5 mins. at 40°C.

The penetration hardness of the products can be measured by means of the ASTM Method D217-52T (Richardson Method). Values obtained for the products of this invention vary from about 70 to about 120 (tenths of a millimetre).

The product stickiness (also spreadability and transferability by rubbing) is determined by rubbing under a 2 kg weight a moulded 1" cylinder of product on a standard cotton cloth (10 cm long) and measuring the amount of product transferred by friction as the cloth is pulled under the weighted cylinder. Suitable products have friction values (transferability factors) of about 100 mg to about 300 mg of product per 10 cm strip of cotton cloth. Preferred products have transferability factors of from above 150 to less than 300.

The product transparency is conveniently measured by means of a lamp/photocell/galvanometer system, reading the percentage of transmitted light after a zero adjustment. Spectrocolorimeters can also be used. Substantially total transparency (i.e. 95%) can be achieved with the products of this invention.

Other relevant properties of the products of this invention are the solidification temperature and viscosity of the product in the fluid state since these are important considerations in processing the compositions into the shaped forms (e.g. sticks) hereinbefore described. These properties have a direct effect on rate of production, size and handling of such shaped forms as well as affecting the transparency and stickiness of the final product. Generally, solidification temperature of the products of this invention range from 40°C to 100°C and the viscosity, as measured by a falling ball viscometer may range from 50 to 3000 cps, most suitable values being in the range from 1000 to 2000 cps.

The following Examples illustrate the invention.

EXAMPLE 1

	Formulation I	Parts	
	Hydrogenated tallow fatty acids	12.5	
	Benzyl alcohol	20.0	
5	Propylene glycol	30.0	5
	Nonionic C ₁₄₋₁₅ alkanols + 11 E.O.	28.0	
	Formulation II	Parts	
	Deionized water	5.0	
10	Low chloride 38% aqueous sodium hydroxide solution	4.1	10
	Formulation III	Parts	
	"Pigmosol Blue 5G"—1% aqueous solution	0.4	
	(PIGMOSOL is a trade mark)		
15	The ingredients of Formulas I and II are separately heated in a mixing tank to 80—85°C with good agitation until homogeneous, and the Formulation II mixture is slowly added with agitation to Formulation I. A few drops of phenolphthalein indicator are then added to the mixture, and if the mixture is still colourless small increments of the sodium hydroxide solution are added till the mixture just turns pink. The Formulation III colour solution is then mixed in, and the mixture held at about 71°C while being poured into stick moulds. The sticks are solidified by cooling carefully and slowly to ensure transparency of the sticks.		15
20			20
25	The resulting transparent, water-soluble, readily spreadable detergent sticks are highly effective for removing stains and soil such as ball pen ink stains, and cuff and collar discolourations, when the stained or soiled areas are rubbed with the sticks and then washed in an aqueous laundry detergent bath. The sticks are stable to varying environmental conditions for extended periods of time.		25
	EXAMPLE 2.		
30	The procedure of Example 1 is repeated with the following formulations, the results being nearly equal:		30

	Formulation I	Parts	
	Hydrogenated tallow fatty acids	10.00	
	Benzyl alcohol	28.65	
	Propylene glycol	28.65	
5	Nonionic C ₁₄₋₁₅ alkanols + 11 E.O.	28.00	5
	Formulation II	Parts	
	Deionized water	4.50	
	35% aqueous sodium hydroxide solution	4.40	
10	Formulation III	Parts	10
	"Pigmosol Blue 5G"—1% aqueous solution	0.10	
	Optiblanc BT11*	0.10	
	("Optiblanc" is a registered trade mark)		
15	Optiblanc 2MG*	0.10	15
	*6% solution of each optical brightener, freed of mineral salts, in 1:1 benzyl alcohol:propylene glycol.		

EXAMPLE 3.

Examples 1 and 2 are repeated except that the nonionic detergent in Formulation I is replaced by an equal amount of the following detergents:

20 (A) Anionic sodium C₁₄₋₁₇ paraffin sulphonate (100% active, pure, desalted)*

(B) 1:1 mixture of (A) and C₁₄₋₁₅ alkanols + 11 E.O.

*Added as a 66.5% solution in 1:1 benzyl alcohol: propylene glycol.

The results are similar to those of Examples 1 and 2. When (A) is employed, it may alternatively be included in Formulation III instead of Formulation I.

25

In the following Examples set forth in Table II, the parts of ingredients are set forth and the identification thereof are given in Table I. The procedure of Example 1 is followed in preparing each of the compositions.

TABLE 1 - INGREDIENTS

COMPONENT A

A1	Hydrogenated tallow fatty acids
A2	Distilled coconut oil fatty acids
A3	Distilled tallow fatty acids
A4	C ₁₁₋₁₃ Synthetic fatty acids
A5	C ₂₂ Fatty acids
A6	Commercial stearic acids
A7	Neat soap (15:85: A2 soap:A3 soap + 33% water)
A8	Soap noodles (85/15 tallow coconut & 12% water)

COMPONENT B

B1	Nonionic reaction product of 1 mole of C ₁₄₋₁₅ primary alkanols with about 11 moles of ethylene oxide (+ 11 E.O.)
B2	Nonionic C ₁₂₋₁₅ primary alkanols + 11 E.O.
B3	Nonionic C ₁₂₋₁₅ primary alkanols + 7 E.O.
B4	Nonionic C ₉₋₁₁ primary alkanols + 5 E.O.
B6	Nonionic C ₁₁₋₁₅ secondary alkanol + 3 E.O.
B7	Nonionic C ₁₆ alkanediol (omega omega) + 5 E.O.
B8	Anionic sodium C ₁₀₋₁₄ (av. dodecyl) alkyl benzene sulphonate
B9	Anionic sodium sulphate of lauryl alcohol + 3 E.O.
B10	Anionic sodium C ₁₄₋₁₇ paraffin sulphonate
B11	Anionic sodium lauryl sulphate
B12	Nonionic C ₈ primary alcohol + 2. E.O.
B13	Nonionic C ₁₂₋₁₄ primary alcohol + 2. E.O.
B14	"Pluronic L-61"
B15	C ₁₆₋₁₈ olefin sulphonate
B16	Nonionic C ₁₁₋₁₅ secondary alcohol + 5 E.O.
B17	Nonionic C ₁₁₋₁₅ secondary alcohol + 7 E.O.
B18	Nonionic C ₁₁₋₁₅ secondary alcohol + 9 E.O.

COMPONENT C

C1	Benzyl alcohol
C2	Lauryl alcohol
C3	Terpineol
C4	Diethyl phthalate
C5	Phenethyl alcohol
C6	Propylene glycol
C7	Ethylene glycol monoethyl ether
C8	Diethylene glycol
C9	Triethylene glycol
C10	Polyethylene glycol M.W. 3000
C11	Triethanolamine
C12	Glycerine
C13	Dipropylene glycol

COMPONENT D

D1	35% aqueous caustic soda solution
D2	Deionized water
D3	49% aqueous caustic soda solution
D4	50% aqueous caustic potash solution

ADDITIVES E

E1	Optical dye
E2	Dye, e.g. "Pigmosol Blue 5G"
E3	Perfume

TABLE II - EXAMPLES

Example	COMPONENTS - PARTS BY WEIGHT				
	A	B	C	D	Additives
4	15 A1	15 B1 20 B17	20 C1 20 C6	5 D2 4.9 D3	
5	10 A1	20 B1 20 B18	20 C1 20 C6	5 D2 3.3 D3	
6	8.5 A1	26.5 BA	23.5 C1 23.5 C10	10 D2 2.9 D3	
7	10.6 A1	27 B19	23.5 C1 23.5 C10 9.4 C12	10 D2 3.2 D3	
7A	10 A1	20 B4 20 B14	15 C1 5 C6 15 C10	1.7 D2 3.3 D3	
8	8 A6	20 B1 20 B18	20 C1 20 C6	2 D2 2.7 D3	
9	10 A1	35 B1	25 C1 23 C6	3 D2 3.303	0.003 E2
10	10 A1	28 B10	28.6 C1 28.6 C6	4.4 D3	0.004 E2
11	12.5 A1	15 B1 20 B8	22.5 C1 22.5 C6	6 D2 4.1 D3	0.004 E2
12	10 A1	30 B1	56 C1	2 D2 4.1 D3	
13	10 A1	35 B1 10 B6	20 C1 5 C6 10 C11	5 D2 3.5 D3	
14	11 A1 11 A2	45.2 B10	11.4 C1 11.4 C6	10.5 D3	
15	11 A1 11 A2	45.2 B1	11.4 C1 11.4 C6	10.5 D3	
16	11 A1 11 A2	45.2 B8	11.4 C1 11.4 C6	10.5 D3	
17	11 A1 11 A2	35.2 B1 10 B8	11.4 C1 11.4 C6	10.5 D3	
18	7 A6	18 B1 16 B10	26.7 C1 26.7 C6	2 D2 3 D3	0.002 E2 0.02 E1
19	8 A1	16 B6 13.3 B10	19.3 C1 19.3 C6	3.6 D1 2 D2	0.004 E2 0.12 E1
20	9 A1	25 B9	27.9 C1 27.9 C6	3.2 D1	0.02 E1 0.004 E2 0.3 E3

TABLE II - EXAMPLES (CONT'D.)

Example	COMPONENTS - PARTS BY WEIGHT				
	A	B	C	D	Additives
21	8 A6	35 B2	25 C1 25 C8	2 D2 2.8 D3	0.002 E2
22	3.5 A1 3.5 A2 3.5 A3	33 B1	26 C1 26 C6	5.1 D1	
23	3 A1 15 A7	28 B1	26 C1 26 C6	1.2 D1	
24	3.5 A1 3.5 A2 3.5 A3	33 B1 12 B10	20 C1 20 C6	5 D1	
25	8 A6	48 B2	20 C1 20 C6	2.8 D2 2 D3	0.005 E1 0.001 E2 0.3 E3
26	8 A6	48 B2	20 C1 20 C6 5 C7	2.8 D2 2 D3 1 D4	0.005 E1 0.001 E2 0.03 E3
27	8 A6	20 B2 20 B13 10 B10	15 C1 10 C6 15 C7	4 D1 1 D4	
28	8 A6	20 B2 10 B10 20 B13	15 C1 10 C6 15 C7	4 D1 5 D2 1 D4	
29	7 A1 7 A2	5 B1 5 B8	37.5 C1 37.5 C6	7 D1	
30	10 A1	14 B1 14 B10	24.6 C1 20.8 C6	4.4 D1 2.4 D2	0.002 E1 0.01 E2 0.3 E3
31	10 A1	28 B2	28.6 C2 28.6 C6	3.2 D1	0.001 E1 0.004 E2 0.3 E3
32	4 A6 5 A8	50 B2	20 C1 20 C6	2.7 D1	0.005 E1 0.003 E2 0.35 E3
33	6 A6 10 A4	20 B2	28 C1 28 C6	8 D1	0.004 E1 0.002 E2 0.35 E3
34	6 A6 10 A4	20 B2	14 C1 14 C4 28 C6	8 D1	0.004 E1 0.002 E2 0.35 E3
35	6 A6	20 B2 10 B16	30 C1 30 C6	3 D1 7 D2	0.004 E1 0.002 E2 0.35 E3

TABLE II - EXAMPLES (CONT'D.)

Example	COMPONENTS - PARTS BY WEIGHT				
	A	B	C	D	Additives
36	5 A5	65 B1	15 C1 15 C6	1.7 D1	
37	10 A5	50 B1 5 B11	20 C5 15 C6	3.3 D4	
38	12 A1	40 B3 15 B7	22 C3 15 C9	6 D2 4 D3	
39	12.5 A1	28 B1	20 C1 30 C6	4 D1 5 D2	
40	3 A6 1 A5	70 B1	20 C1 6 C6	1.3 D1 2 D2	
41	5 A1	37.5 B1 37.5 B19	15 C1 5 C6	1.7 D1 2.5 D2	
42	10 A1	70 B2	15 C1 5 C6	5.1 D1 2 D2	

EXAMPLE 43.

Examples 1, 2 and 3 are repeated with similar results, when the hydrogenated tallow fatty acids in Formulation 1 are replaceably,

(A) Distilled coconut oil fatty acids

(B) 1:1 mixture of (A) and hydrogenated tallow fatty acids

(C) Commercial stearic acid

(D) 1:1 mixture of (A) and (C)

(E) Palmitic acid

(F) 1:1 mixture of (E) and hydrogenated tallow fatty acids

EXAMPLE 44

Examples 1-4 are repeated, with similar results, when the benzyl alcohol is replaced by an equivalent amount of phenethyl alcohol and the propylene glycol by an equivalent amount of polyethylene glycol, M.W. 3000.

WHAT WE CLAIM IS:—

1. A detergent composition capable of being formed into water-soluble (as hereinbefore defined), spreadable, form-stable, solid shaped articles, comprising: (I) a matrix of (A) a soap component, (B) a synthetic detergent component and (C) a solvent component.

the soap component (A) constituting from 2 to 25% of the matrix and comprising an alkali metal, alkaline earth metal, ammonium or amine salt of a C_{8-30} fatty acid or a mixture of such soaps, the soap component providing in the matrix not more than 20% of salts (other than potassium salts) of fatty acids of 18 or more carbon atoms or not more than 40% of potassium salts of such acids, and wherein the soap has a weighted average carbon content (as hereinbefore defined) of at least C_{14} ;

the synthetic detergent component (B) constituting from 5 to 88% of the matrix and comprising at least one water-soluble member of the group consisting of anionic organic sulphonates, carboxylates and phosphonates, anionic alcohol sulphates, carboxylates and phosphates, anionic ether sulphates, carboxylates and phosphates, anionic acyl sarcosinates, isethionates and taurides, and nonionic aliphatic detergents, but a maximum of 50% when the synthetic detergent component consists only of anionic organic sulphonates or anionic alcohol sulphates or mixtures thereof;

and the solvent component (C) constituting from 10 to 70% of the matrix and comprising at least one normally liquid, substantially non-volatile organic solvent having a boiling point of at least 100°C, at least 10% of component (C) being water-insoluble; and

5 (II) a water component (D) constituting from 1 to 35 parts per 100 parts of the matrix. 5

2. A composition as claimed in Claim 1 wherein the matrix contains from 4 to 15% of component (A), from 25 to 76% of component (B) and from 20 to 60% of component (C), the composition containing from 1 to 15% of water as component (D). 10

3. A composition as claimed in Claim 1 or Claim 2 the fatty acids average at least 12 carbon atoms per molecule.

4. A composition as claimed in any of the preceding claims wherein component (A) comprises alkali metal salts of a mixture of palmitic and stearic acids.

15 5. A composition as claimed in any of Claims 1 to 3 wherein at least 40% of component (A) is constituted by alkali metal salts of hydrogenated tallow fatty acids. 15

6. A composition as claimed in any of the preceding claims wherein at least 40% of component (B) is an aliphatic nonionic detergent.

20 7. A composition as claimed in Claim 6 wherein the aliphatic nonionic detergent is a reaction product of from 2 to 50 moles of ethylene oxide with 1 mole of C₈₋₂₀ saturated aliphatic alcohol. 20

25 8. A composition as claimed in any of the preceding claims wherein at least 40% of component (B) is an anionic alkali metal, ammonium or amine salt of an alkylaryl sulphonic acid, an alphaolefin sulphonic acid, a paraffin sulphonic acid, an alcohol sulphate or a sulphate ester of the reaction product of from 1 to 20 moles of ethylene oxide with 1 mole of a reactive hydrogen-containing compound of from 8 to 24 carbon atoms. 25

30 9. A composition as claimed in any of the preceding claims wherein at least 10% of the nonvolatile solvent is constituted by water-soluble dihydric alcohol. 30

10. A composition as claimed in Claim 9 wherein the substantially water-insoluble portion of the solvent component (C) comprises benzyl alcohol and the water-soluble portion of the solvent component (C) comprises propylene glycol.

35 11. A composition as claimed in Claim 10 containing substantially equal amounts of the water-insoluble and water-soluble portions of the solvent component (C). 35

40 12. A composition as claimed in any of the preceding claims wherein the matrix contains from 0.8 to 5.7 parts of component (B) per part of component (A), from 1 to 8.6 parts of component (C) per part of component (A) and from 0.53 to 6.8 parts of component (C) per part of component (B). 40

13. A composition as claimed in any of the preceding claims containing from 0.1 to 5% by weight of a free alkali metal hydroxide.

45 14. A composition as claimed in Claim 1, substantially as described in any of the Examples. 45

50 15. A method of preparing a composition as claimed in any of the preceding claims comprising melting the free fatty acids of the soap component (A), mixing the molten fatty acids with the solvent component (C) to produce a homogeneous liquid, and admixing therein, at a temperature above the melting point of the free fatty acids and in the presence of components (B) and (D), sufficient alkali metal-, alkaline earth metal-, ammonium- or amine-salt forming bases to saponify and/or to neutralize the fatty acids and form their alkali metal, alkaline earth metal, ammonium or amine salts *in situ*. 50

55 16. A method of preparing a composition as claimed in any of Claims 1 to 14 comprising melting the free fatty acids of the soap component (A), mixing the molten fatty acids with the solvent component (C) and any nonheat-sensitive detergent of component (B) at a temperature above the solidification point of the mixture, admixing therein, at that temperature and in the presence of component (D), sufficient alkali metal-, alkaline earth metal-, ammonium, or amine-salt forming base to saponify and/or neutralize the fatty acids and form their alkali metal, alkaline earth metal, ammonium, or amine salts *in situ*, cooling the resulting liquid to just above the solidification point of the salts, and then admixing therein any heat-sensitive detergent of component (B). 60

17. A method as claimed in Claim 15 or Claim 16 wherein the salt-forming base is an alkali metal hydroxide.

18. A detergent composition as claimed in any of the Claims 1 to 14 which has been prepared by a method as claimed in any of Claim 15 to 17.

19. A water-soluble, spreadable, formstable, solid detergent stick (as hereinbefore defined) comprising a composition as claimed in any of Claims 1 to 14 or 18.

20. A method of cleaning a soiled surface comprising applying thereto a composition as claimed in any of Claims 1 to 14 or 18, and then washing the surface with an aqueous detergent solution.

21. A method of cleaning a soiled surface comprising contacting the surface with a detergent stick as claimed in Claim 19 to transfer the composition to the surface, and then washing the surface with an aqueous detergent solution.

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